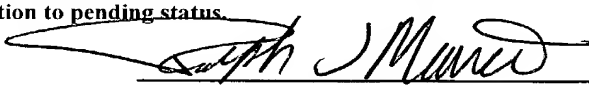


FORM PTO-1390 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER ACR6100US	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	
INTERNATIONAL APPLICATION NO. PCT/US99/31246		INTERNATIONAL FILING DATE 30 December 1999		PRIORITY DATE CLAIMED 09/869931 31 December 1998	
TITLE OF INVENTION Cationic Gemini and Related Multiple Hydrophilic/Hydrophobic Functional Compounds...					
APPLICANT(S) FOR DO/EO/US S. Mirviss, D. Steichen, P. Spellane & H. Cho					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is attached hereto.</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (unsigned)</p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11 to 20 below concern document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input type="checkbox"/> A FIRST preliminary amendment.</p> <p>14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information: Petition under 37 CFR 137</p>					
Express Mail Label No.: EM122096140US					

09/869931 U.S. APPLICATION NO. (37 CFR 1.53)		INTERNATIONAL APPLICATION NO. PCT/US99/31246		ATTORNEY'S DOCKET NUMBER ACR6100US	
21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY	
				\$ 100.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	32 - 20 =	12	x \$18.00	\$ 216.00	
Independent claims	4 - 3 =	1	x \$80.00	\$ 80.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 396.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
SUBTOTAL =				\$ 396.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 396.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$ 396.00	
				Amount to be refunded:	\$
				charged:	\$
a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>01-1350</u> in the amount of \$ <u>396.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1350</u> . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO Ralph J. Mancini Akzo Nobel Inc. Intellectual Property Department 7 Livingstone Avenue Dobbs Ferry, NY 10522-3408 (914) 674-5465			 SIGNATURE Ralph J. Mancini NAME 34,054 REGISTRATION NUMBER		

09/869931

~~Cationic Gemini and Related Multiple Hydrophilic/Hydrophobic Functional~~
~~Compounds and Their Use As Surfactants~~

5

Field of Invention

The present invention generally relates to improved multiple hydrophilic/hydrophobic functional quaternary ammonium compounds "multiple functional" surfactants, useful in detergents and personal care, mining, industrial, and catalyst products, in biocidal compositions at higher concentrations, and as emulsifiers.

15 Background of The Invention

Conventional surfactants have one hydrophilic group and one hydrophobic group. Dimeric surfactants which are commonly called "Gemini" surfactants are those which comprise two hydrophilic functional groups and two hydrophobic functional groups. Gemini surfactants have unique physical properties resulting from constraint of two hydrophilic groups in close proximity and the consequent micellar properties, which has led to an intensive study of Gemini surfactants as detergents, softeners, emulsifiers, phase transfer catalysts, biocides, and as components in skin care lotions, hair conditioning compositions and cosmetics compositions. Their use is also being investigated in ore flotation, oil well drilling and in other industrial applications.

It is therefore an object of the present invention to provide a novel class of cationic multiple functional surfactants that have application in the treatment of textile fibers to provide softeners and static control.

It is also an object to provide a class of multiple functional surfactants having improved detergency at extremely low concentrations, while at the same time being highly biodegradable.

35

It is also an object of the present invention to provide a class of multiple functional surfactants which are useful as emulsifiers, phase transfer catalysts, biocides, in ore flotation, in oil well drilling and in other related applications.

5

Finally, it is an object of the invention to provide a class of multiple functional surfactants which are useful in skin care lotions, hair conditioning compositions and cosmetics compositions at low concentrations.

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These and other objectives are realized by the compositions and methods of the present invention.

Summary of the Invention

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The present invention generally relates to several new classes of cationic multiple functional surfactants and to compositions containing same. The invention also relates to various processes for preparing the multiple functional surfactants of the present invention.

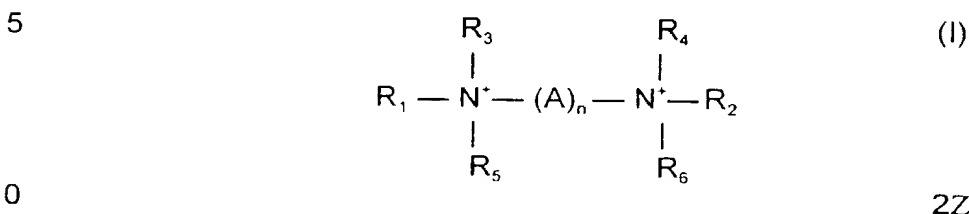
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Detailed Description of The Present Invention

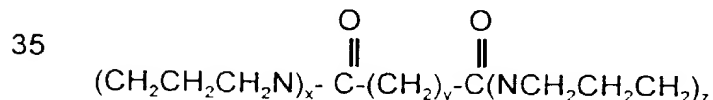
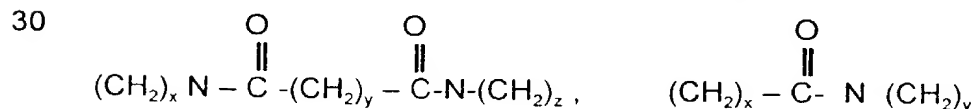
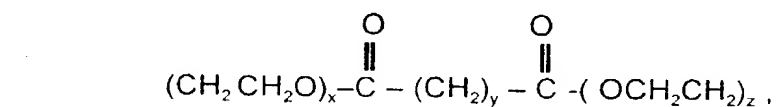
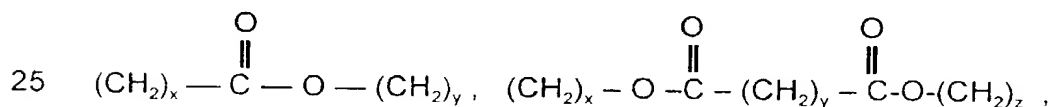
The present invention generally relates to multiple functional surfactants of the formulae I-IV, below, to compositions containing same and to methods for their preparation. The beneficial features of the multiple functional surfactants of the present invention derive from their multiple functional character, i.e., the chemical species of the present invention contain two or more hydrophobic groups and two or more hydrophilic groups in each molecule.

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- I. Multiple functional quaternary ammonium compounds containing ester or amide spacer group(s) of the general formula:



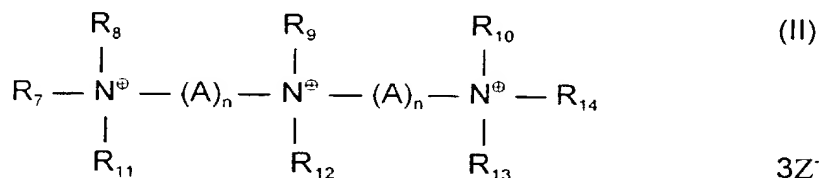
wherein R_1 and R_2 are the same or different and are selected from straight or branched chain, substituted or unsubstituted C_1 - C_{22} alkyl or alkenyl groups wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage, or mixtures thereof; R_3 , R_4 , R_5 , and R_6 are the same or different and are selected from straight or branched chain, substituted or unsubstituted C_1 - C_{22} alkyl or alkenyl groups wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage, or mixtures thereof; and A is a spacer selected from the group consisting of :



or other ester - or amide-functional alkyl groups in the spacer,

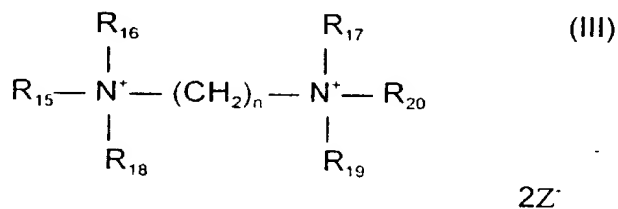
wherein each of x, y and z can independently be an integer of 1-20; and n is an integer of from 1-20;

II. Multiple functional quaternary ammonium compounds with ester or amide spacer group(s) of the general formula:



wherein R₇, R₈, R₉, R₁₀, R₁₁, R₁₂, R₁₃, and R₁₄ are the same or different and are selected from straight or branched chain, substituted or unsubstituted C₁-C₂₂ alkyl or alkenyl groups, wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage, or mixtures thereof; and A is a spacer group as defined above, and wherein x, y and z are each independently an integer of 1-20; and n is an integer of from 1-20; or

III. Asymmetric multiple functional quaternary ammonium compounds:



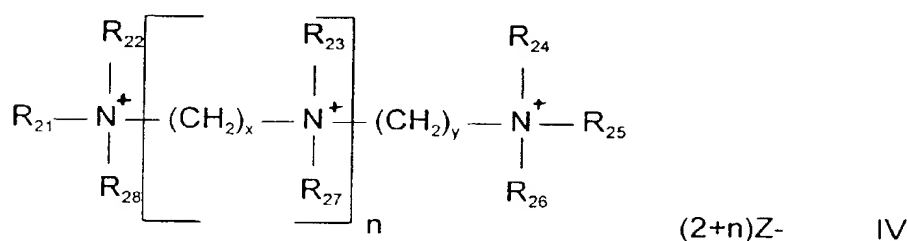
wherein R₁₅ and R₂₀ are different and are selected from straight or branched chain, substituted or unsubstituted C₈-C₂₂ alkyl or alkenyl groups wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage, or mixtures thereof; R₁₆, R₁₇, R₁₈

and R_{19} are the same or different and are selected from straight or branched chain, substituted or unsubstituted C_1 - C_{22} alkyl or alkenyl groups wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage, or mixtures thereof; and n is an integer of from 1-20.

IV. Symmetric "gemini" quaternary ammonium compounds prepared in the reaction of alkyl multiple amine compounds with long chain aldehyde or alcohols of the general formula IV

10

15



wherein R_{21} , R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , and R_{28} are the same or different and are selected from straight or branched chain, substituted, or unsubstituted C_1 - C_{22} alkyl or alkenyl groups, wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage or mixtures thereof, and where x and y are each independently an integer of from 1-20 and n is an integer from 0-20; wherein in each of I, II, III and IV, Z^- is an anion.

25

In each of formulae I-III, above, R_1 , R_2 , R_7 , R_{14} , R_{15} and R_{20} are preferably selected from C_8 - C_{18} alkyl groups, optionally containing an ester linkage. It is also preferred that x , y and z are 0-5 and that n is 1-10.

30

In formula IV above R_{21} and R_{25} are preferably selected from 2-ethylhexyl, nonyl-alkyl, or a C_{13} - C_{15} mixed alkyl group, and R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , and R_{28} independently selected from methyl, ethyl, or propyl, and $n = 0, 1$, or 2 .

Concerning the multiple functional quaternary ammonium compounds of formula I, it is preferred that R_1 and R_2 be selected from 2-ethylhexyl, nonyl-alkyl, a $C_{13} - C_{15}$ mixed alkyl group, or from the group consisting of dodecylalkyl, hexadecylalkyl, octadecylalkyl, oleylalkyl, cocoalkyl, soyaalkyl, tallowalkyl, or hydrogenated tallowalkyl; that R_3 , R_4 , R_5 and R_6 be independently selected from methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, or a $C_{13} - C_{15}$ mixed alkyl group; and that n be an integer of from 1 to 5.

10

In the multiple functional quaternary ammonium compounds of formula II, it is preferred that each of R_7 , R_8 , R_9 , R_{10} , R_{11} , R_{12} , R_{13} and R_{14} are independently selected from methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, a $C_{13} - C_{15}$ mixed alkyl group, or from the group consisting of dodecylalkyl, hexadecylalkyl, octadecylalkyl, oleylalkyl, cocoalkyl, soyaalkyl, tallowalkyl, or hydrogenated tallowalkyl; and that n be an integer of from 1 to 5.

Finally, it is preferred that, in the asymmetrical multiple functional quaternary ammonium compounds of formula III, R_{15} , R_{16} , R_{17} , R_{18} , R_{19} and R_{20} be selected from methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, a $C_{13} - C_{15}$ mixed alkyl group, or from the group consisting of dodecylalkyl, hexadecylalkyl, octadecylalkyl, oleylalkyl, cocoalkyl, soyaalkyl, tallowalkyl, or hydrogenated tallowalkyl or other long chain fragment with the proviso that the group of substituents on one N^+ be not identical to the group of substituents which surround the other N^+ center and that n is an integer of from 1 to 20.

The ester or amide containing multiple functional compounds of the present invention exhibit enhanced biodegradability which is extremely desirable for obvious environmental reasons. For example, enhanced biodegradability is a desired attribute in fabric softening

compositions and in other uses where the content and volume of waste water effluent streams needs to be controlled.

When used in a fabric softening composition, the compounds of
5 the present invention are preferably delivered to the textile to be softened in amounts effective to impart the desired softness and/or anti-static properties to said textile(s). Said effective amount typically ranges in an amount of from about 0.5 to 3 grams of softening compound(s) per average load of laundry.

10

Delivery of the compounds of the present invention to the textile to be treated can be conducted by various means. For example, the compounds of the present invention can be formulated into liquid softening compositions, solid formulations and/or solid articles. In a liquid
15 formulation, the compounds of the present invention are dissolved and/or suspended in water, wherein said formulation optionally also contains other conventional softeners as well as other ingredients and diluents such as detergents, optical brighteners, viscosity aids, soil release agents, fragrance, and the like, in the requisite amounts so to provide an
20 effective amount of the compounds of the present invention to the textile to be treated.

With solid formulations, the multiple functional surfactants of the present invention are formed into small flowable particles or beads on a
25 water-soluble carrier such as a solid detergent, which is optionally compounded with builders, brighteners, fragrance and the like.

Finally, the multiple functional surfactants of the present invention can be combined with a distribution agent and applied, or coated on a
30 solid carrier such as a woven, or non-woven fabric or bonded polyester

sheet. Alternatively, the composition can be inserted into a container designed for insertion into a clothes dryer.

The present invention also relates to various methods for the preparation of multiple functional surfactants. For example, the multiple functional surfactants of formula I which contain ester spacer groups can be prepared by reacting a dialkylalkanol amine of formula



wherein each of Q_1 , Q_2 and Q_3 is independently selected from the group consisting of C_1 - C_{22} alkyl groups and a dicarboxylic acid of the formula



wherein n is an integer of from 1-12, to form a reaction mixture, or a diester of same, and thereafter quaternizing the reaction mixture.

The dialkylalkanol amine is preferably prepared by ethoxylating a fatty amine compound of the formula



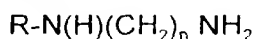
Wherein Z is a C_{12} - C_{22} substituted or unsubstituted, saturated or unsaturated, straight or branched chain alkyl group, and Y is a C_1 - C_{22} substituted or unsubstituted, saturated or unsaturated, straight or branched chain alkyl group.

Preferably, the fatty amine compound is selected from the group consisting of dodecylamine, hexadecylamine, octadecylamine, oleylamine, cocoalkylamine, soyaalkylamine, tallowalkylamine, hydrogenated tallowalkyl amine, dicocoalkylamine, ditallowalkylamine, dihydrogenated tallowalkylamine, dioctadecylamine, and mixtures thereof.

The dicarboxylic acid employed is preferably selected from the group consisting of oxalic, malonic, succinic, glutaric, adipic, maleic, fumaric and

mixtures thereof. The most preferred dicarboxylic acid is adipic acid, or mixed short chain di-acids which are commercially available from, for example, DuPont.

- 5 The multiple functional surfactants of formula I which contain an amine-functional spacer group can be prepared in the reaction of an N-alkylamino fatty amine compound



with a dicarboxylic acid or mixtures of dicarboxylic acids(or diesters of same).

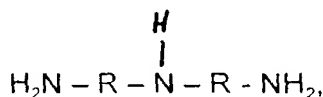
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The multiple functional quaternary ammonium compounds of Formula IV can be prepared by reacting a bis-primary amine alkane (e.g., hexamethylenediamine) with two equivalents of aldehyde, e.g., 2-ethylhexanal, or other long chain aldehydes such as nonanal or mixed

- 15 C₁₃-C₁₅ aldehydes (which are commercially available).

Other multiple functional quaternary ammonium surfactants of general Formula IV of the present invention can be prepared by reaction of aliphatic triamines of formula:

20



- wherein R is a saturated or unsaturated hydrocarbon group, with
 25 aldehyde, e.g., 2-ethylhexanal, or longer chain aldehyde such as nonanal or mixed C₁₃-C₁₅ aldehydes (which are commercially available), or an alcohol. For example, tris-quaternary ammonium surfactants can be prepared by reaction of bis(hexamethylene) trimine with alkylaldehyde, such as 2-ethylhexanal, followed by methylation and quaternization.

30

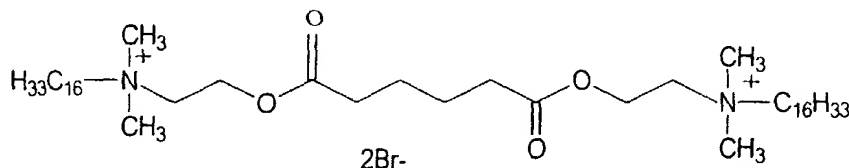
The cationic gemini and related multiple functional hydrophilic/hydrophobic functional compounds of the present invention can be employed alone, or in combination with typical surfactants,

including mono-quaternary ammonium compounds. When employed in combination with mono-quaternary ammonium compounds, it has been found that as little as 5-10% of the compounds of the present invention can reduce the Critical Micelle Concentration (CMC) from 10 up to 100 fold. CMC is a measurement employed to determine the effectiveness of a surfactant composition. The lower the CMC values, the better the surfactant. Thus, by using small amounts of the surfactants of the present invention in combination with conventional surfactants, the addition rates of the conventional surfactants can be greatly reduced.

The present invention shall now be illustrated by the following non-limiting examples.

Example 1 - Preparation of a Multiple Functional Quaternary Ammonium

Compound with Ester-functional Spacer Groups



Preparation of $(CH_2)_{14}(CO_2CH_2CH_2NMe_2)_2$ from adipic acid and dimethylethanolamine in toluene

Procedure - A 1 L round bottom flask was charge with 14.6 g of adipic acid (1.00 mole), 196.0 g of dimethylethanolamine (2.20 mole - 10% excess), 300 mL toluene and 1.5 g of p-toluenesulfonic acid. The reaction mixture was heated to reflux with stirring. A Dean-Stark trap was attached to one neck of the 4-neck flask and to a water condenser. The reaction was heated at reflux for a total of 22 hours as 54.5 mL H_2O distilled. The product was stripped of solvent on a rotary evaporator at 80° C and 15 mm Hg. The product weighed 270.6 g. Infrared spectroscopy of product indicated only the ester.

Reaction of $(CH_2)_{14}(CO_2CH_2CH_2NMe_2)_2$ with hexadecyl bromide

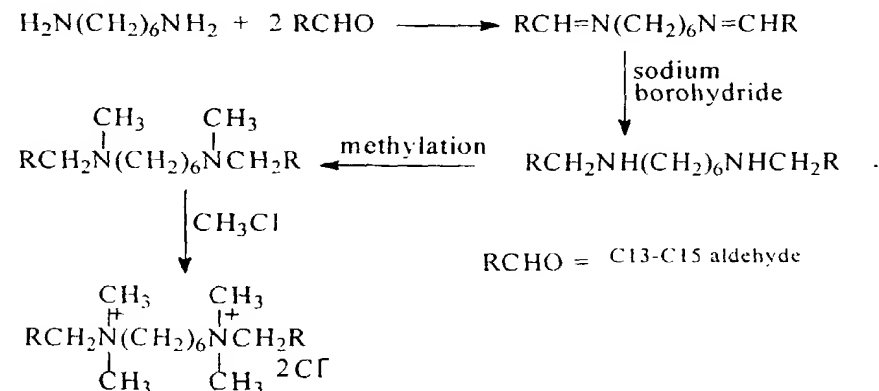
Procedure - A 1 L Morton flask was charged with 57.6 g of $(\text{CH}_2)_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2$ (0.2 mole) and 300 mL of monoglyme. 122.0 g $\text{C}_{16}\text{H}_{33}\text{Br}$ (0.4 mole) were added with stirring. The mixture was heated to 85°C with stirring under an N_2 atmosphere and maintained for 73 hours.

- 5 No solid was evident at the conclusion of heating but did form on standing over several days. The total product was suction filtered and the beige solid was sucked dry. It was then washed twice with diethylether and again sucked dry, then let stand in a crystallization dish overnight. The solid product weighed 135.5 g (theoretical yield: 179.6 g). Another 30.8 g
- 10 solid product was reclaimed from the filtrate for an overall yield of 92.6%. NMR analysis of product indicated 80 mole % purity of diquaternary compound, 14 mole % mono-quaternary and 6 mol % mono-quaternary-monoacid product.

- A composition was prepared comprising 90% Arquad® 12
- 15 (available from Akzo Nobel Chemicals Inc., Chicago, IL) and 10% of the compound of example 1. This composition exhibited a 50 fold reduction of CMC values compared to a composition comprising 100% Arquad® 12.

- 20 Example 2 – Preparation of Multiple Functional Quaternary Ammonium Compound in Reaction of Aldehyde with Alkyl-diamine: reaction of 1,6-hexanediamine with mixed $\text{C}_{13}/\text{C}_{15}$ aldehyde, followed by reduction, methylation, and quaternization

Summary:



1. Reaction of 1,6-hexanediamine with mixed C₁₃/C₁₅ aldehyde. The mixed aldehyde was used as obtained from Celanese Ltd. Chemicals Division (Dallas, TX); the average molecular weight was estimated to be 211. The aldehyde mixture (400 g., 1.89 moles)
5 was added in portions to melted 1,6-hexanediamine (107 g., 0.92 mole). The reaction was exothermic and was therefore cooled occasionally. The product was washed with water; after solvent was removed by evaporation, a oily yellow liquid (428 g.) was obtained.
10
2. Sodium borohydride (32 g.) was added as powder to a solution of the bis-imine compound (404 g., product in 1 above). The reduction reaction was followed by observing disappearance of the imine carbon's ¹³C NMR. The reaction mixture was washed
15 thoroughly with water before solvent was removed by evaporation. The product was a pale yellow liquid (400 g.)
3. Methylation of the bis-secondary-amine by Eschweiler-Clarke procedure (see also Leukhart Reaction, Organic Reactions,
20 Volume 5, p. 323). To the bis-sec-amine (360 g., 0.71 mole) 90% formic acid was added slowly, forming a light brown solution as the reaction temperature increased to 75° C and then cooled to 50-60° C. The 37% formaldehyde (66 g., 0.814 mole) was slowly added as CO₂ gas evolved. The mixture was heated until gas evolution
25 ceased. Ca. 80 g. of concentrated HCl was added, and the formic acid and any excess formaldehyde were removed at 65° C on a rotary evaporator. The residue was dissolved in water and neutralized with 25% aqueous NaOH (ca. 65 g.). The product was washed with water and dried. A pale yellow liquid (440 g.) was
30 obtained and identified as the bis-tertiary amine.

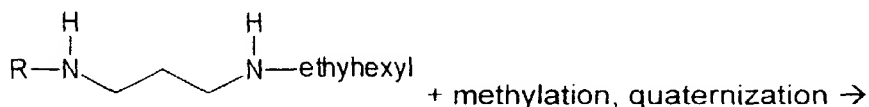
4. Quaternization of the bis-tertiary amine compound prepared in 3 above. In a 1-liter titanium autoclave, a solution of bis-tertiary-amine in methanol (150 g) with sodium bicarbonate was purged with nitrogen and heated with methyl chloride at about 80°C until
- 5 all amine had been consumed (in about 10 hours). Filtration and evaporation yielded a brownish yellow thick paste (215 g.) that was identified as the bis-quaternary ammonium compound.

10 Example 3 - Preparation of Asymmetric Multiple Functional Quaternary Ammonium Surfactant Compounds

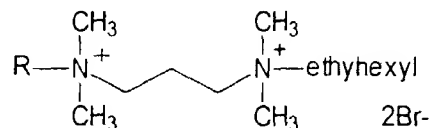
- Asymmetric dimeric- or higher oligomeric surfactant compounds are prepared from Duomeen®, Triameen®, and Tetrameen® compounds
- 15 available from Akzo Nobel Chemicals Inc., Chicago, IL, using an amine-aldehyde condensation reaction.



- 20 Duomeen
where R = coco-, tallow-, or oleylalkyl



25



- 30 Example 4 – Preparation of Multiple Functional Quaternary Ammonium Compound in the reaction of bis(hexamethylene)triamine with mixed C₁₃/C₁₅ aldehyde, followed by reduction, methylation, and quaternization

- 1 The mixed aldehydes were added in portions to melted
bis(hexamethylene)triamine; and the exothermic reaction was
cooled. The reaction mixture was washed with water, then solvent
removed by evaporation to yield the bis-imine mono -secondary
5 amine compound, a pale yellow liquid.
2. Reduction of the bis-imine-mono-sec-amine compound with
sodium borohydride. The bis-imine compound (283 g.) prepared in
1 above was dissolved in 150 g. methanol. To this 25 g. sodium
10 borohydride was added in small portions until the reduction was
complete. The reduction reaction was followed by observing
disappearance of the imine carbon's ^{13}C NMR. The reaction
mixture was washed thoroughly with water before solvent was
removed by evaporation. The product was a pale yellow liquid
15 (247 g.)
3. Methylation of the tris-secondary amine compound prepared in 2
above. The tris-sec-amine compound (245.6 g., 1.17 mole). To
this solution, formic acid was added slowly, forming a light brown
20 solution as the reaction temperature increased to 75° C and was
then cooled to 50-60° C. The 37% formaldehyde (66 g., 0.814
mole) was slowly added as CO_2 gas evolved. The mixture was
heated until gas evolution ceased. Ca. 80 g. of concentrated HCl
was added, and the formic acid and any excess formaldehyde
25 were removed at 65° C on a rotary evaporator. The residue was
dissolved in water and neutralized with 25% aqueous NaOH (ca.
65 g.). The product was washed with water and dried. A pale
yellow liquid (247 g.) was obtained and identified as the tris-tertiary
amine.

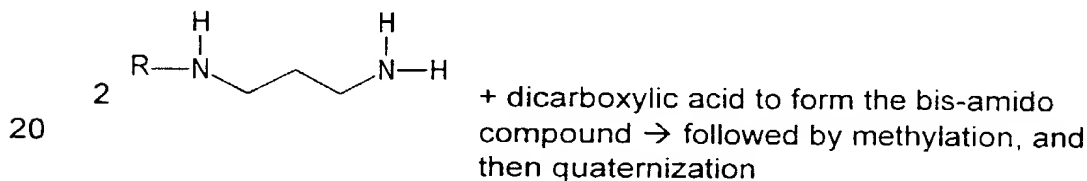
30

- 4 Quaternization of the tris-tertiary amine compound. The tris-tert-amine prepared in 3 above was quaternized in a procedure like those described elsewhere in this application. In a 1-liter titanium autoclave, a solution of tris-tertiary-amine in methanol (155 g. compound in 150 g. methanol) with sodium bicarbonate was
 5 purged with nitrogen and heated with methyl chloride at about 80°C until all amine had been consumed (in about 10 hours). Filtration and evaporation yielded a brownish yellow thick paste (210 g.).

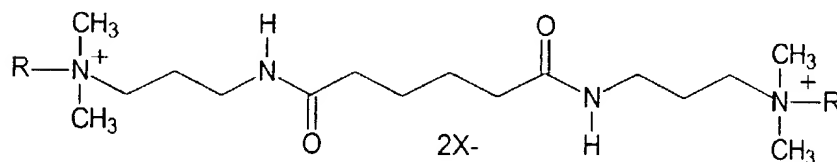
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Example 5 - Preparation of Amido-Bridged Multiple Functional Quaternary Ammonium Surfactant Compounds

- 15 Dimeric - or higher multiple functional surfactant compounds with amide groups in the spacer groups are prepared from Duomeen®, Triameen®, and Tetrameen® compounds from Akzo Nobel Chemicals, Inc. in the following manner:



where R = coco-, tallow-, or oleylalkyl



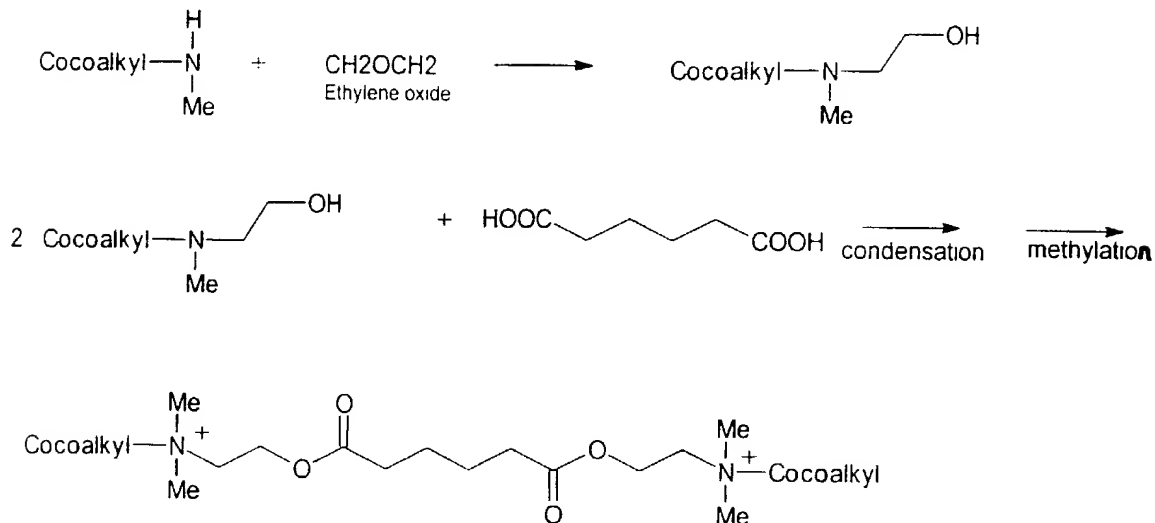
25 R = coco-, tallow-, or oleylalkyl

Example 6 -- Preparation of Multiple Functional Quaternary Ammonium Surfactant Compounds With Ester-Groups in the Spacer from Ethoxylated Fatty Amine Compounds

30

Various mono- and di-alkyl fatty amine compounds are available from Akzo Nobel Chemicals, Inc. and are useful as starting materials. The

following route to a di-ester linked multiple functional quaternary ammonium compound can usefully be employed.



5

Example 7 Reaction of Ethoxylated Armeen 2HT with Succinic Acid, Followed by Quaternization

- 10 Ethoxylation of dialkylamine, followed by reaction with dicarboxylic acid and methylation, will yield the bis-ester-spaced bis(methyldialkylammonium) compound.

1. Ethoxylation of Armeen 2HT

15

In a 1-liter autoclave, Armeen 2HT (234.7 g, 0.5 mole) was dissolved in isopropyl alcohol (80 g) by heating. After nitrogen purging, ethylene oxide (22g, 0.5 mole) was introduced. The mixture was heated at 80°C for two hours. The ¹³C NMR indicated that the reaction was good except
 20 that some starting amine remained unreacted (HN-CH₂- at 50.24 ppm). Additional 11 g of ethylene oxide was added, and the heating at 80°C continued for two more hours. After evaporation, a white solid paste (250 g) was obtained. The product, ethoxylated Armeen 2HT, consisted of monoethoxylated amine, 71.3 mole %; polyethoxylated amine, 26.0 mole
 25 % with n = 2.7; and unreacted amine, 2.7 mole %.

2. Reaction of Ethoxylated Armeen 2HT with Succinic Acid

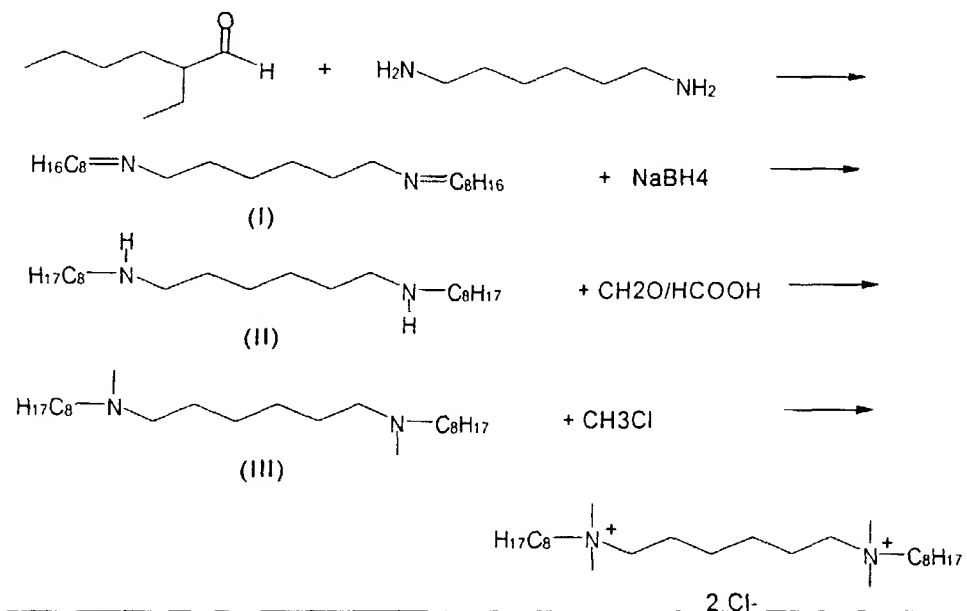
Under an atmosphere of nitrogen, a mixture of ethoxylated Armeen 2HT (172 g, 0.3 mole), succinic acid (17.84 g, 0.15 mole) and 50% aqueous hypophosphorous acid (0.74 g) was heated with stirring at 180-5°C for 5 hours. An off-white thick paste was obtained. The product consisted of the desired diamine esters 90% and monoamines which accounted for 10% by weight.

10 3. Quaternization of Bis-(ethoxylated Armeen 2HT) Succinate Diester

To a solution of bis-(ethoxylated Armeen 2HT) succinate (89 g, 0.14 equiv) in isopropyl alcohol (20 g) at 75-80°C, dimethyl sulfate (about 17 g, 0.135 mole) was slowly added. Free amine should be about 2% indicating substantial completion of quaternization. Evaporation yielded the neat ester diquaternary ammonium compound.

Example 8 PREPARATION OF BIS(2-ETHYLHEXYLDIMETHYLAMMONIUM)-1,6-HEXANE DI(CHLORIDE) VIA BIS(SCHIFF BASE) INTERMEDIATE

Summary



1. Reaction of 2-Ethylhexanal with 1,6-Hexanediamine

To the melt 1,6-hexanediamine (58.1 g, 0.5 mole) at ca. 50° C, 2-ethylhexanal (128.2 g, 1 mole) was slowly added with stirring over three hours. Cooling in an ice-water bath occasionally was necessary because the reaction was exothermic. The reaction was completed as indicated by the disappearance of the aldehyde carbon in the ¹³C NMR spectrum. The reaction product was washed several times with deionized water. Evaporation yielded a yellow liquid (ca 160 g) in nearly quantitative yield.

2. Reduction of Diimine with Sodium Borohydride

To a solution of the diimine (I) (141.6 g, 0.38 mole) in methanol (150 g) sodium borohydride (ca 20 g) was added in small portions. During the addition, the reaction flask was cooled in an ice water bath from time to time. The reaction was completed as indicated by the disappearance of the imine carbon line at 168 ppm in the ¹³C NMR spectrum. The reaction mixture was washed with deionized water several times. Evaporation gave a yellowish liquid (ca 138 g).

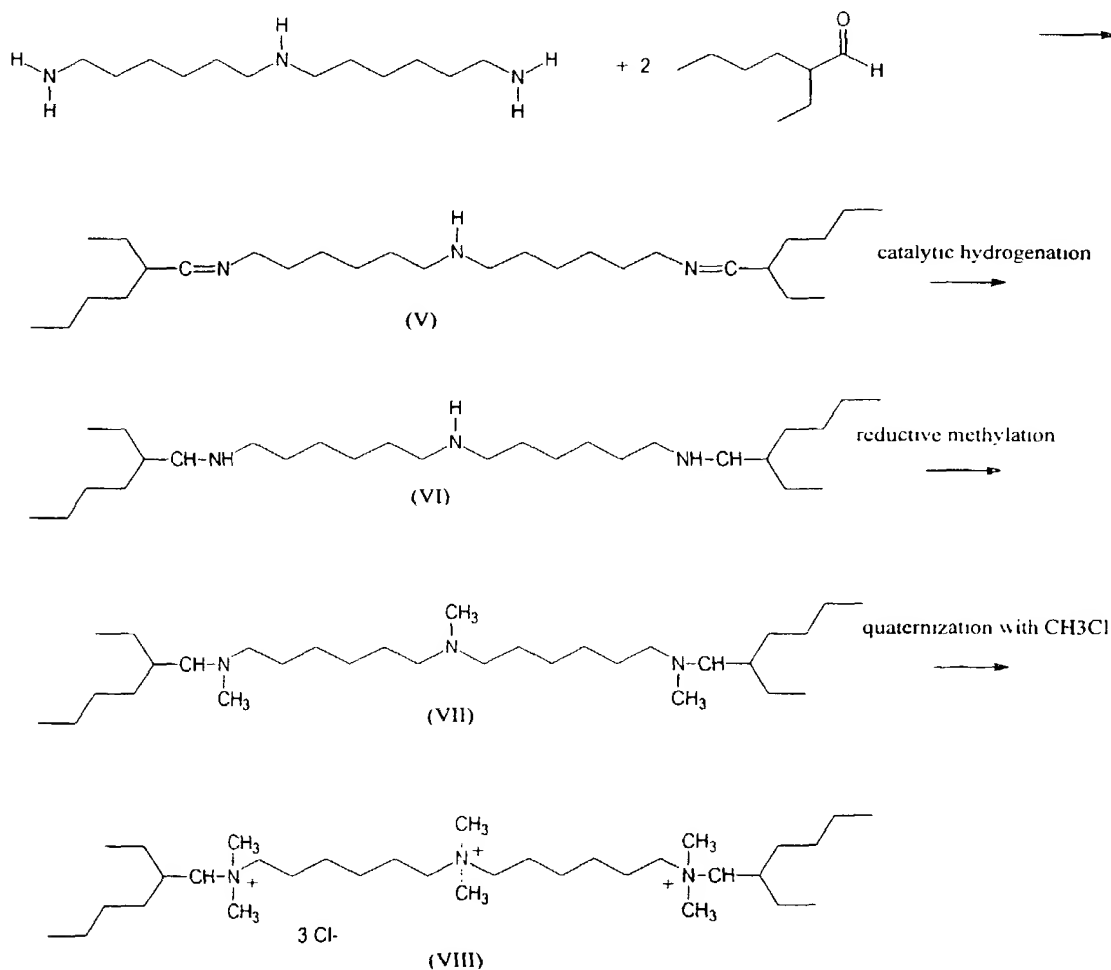
3. Methylation of N,N'-Di(2-ethylhexyl)-1,6-hexanediamine

The addition of 90% formic acid with stirring to the diamine (II) (126.3 g, 0.37 mole) yielded a light brown solution as the temperature rose to 75° C. Having been cooled to room temperature the mixture was treated with 37.1% formaldehyde solution (65.8 g, 0.814 mole) by adding the formaldehyde in small portions with stirring. The resulting mixture was evaporated on a rotary evaporator at ca 65° C for 2 hours. About 72 g of concentrated HCl was then added. The mixture was heated at 70° C for 3 hours and was then neutralized with 25% aqueous NaOH solution. The product was washed with water several times and evaporated to yield a pale yellow liquid (ca 150 g).

4. Quaternization of the di-tertiary-amine (III) with Methyl Chloride

A solution of di(tertiary amine) (147.5 g, 0.4 mole) was quaternized with methyl chloride in the presence of sodium bicarbonate (15 g), at 80° C for about 10 hours. The reaction was completed as indicated by the disappearance of the peak of the methyl carbon on nitrogen at 42.7 ppm in the ^{13}C NMR spectrum. The reaction mixture was filtered and the filtrate was evaporated to yield the desired diquaternary ammonium salt, a pale yellow paste (189 g).

Example 9 – Preparation of bis(2-ethylhexyldimethylammonium) (dimethylammonium) dihexane trichloride Summary



1. Reaction of di(hexamethylene)triamine with 2-Ethylhexanal

Note that the "triamine" is actually a mixture of triamine and 1,6-hexanediamine. NE (neutralization equivalent) of primary amine = 96.46;

5 NE(secondary amine) = 341.76. 86% triamine, 14% diamine.

The mixture of "triamine" (101.4 g, 1.05 equivalents primary amine) and 2-ethylhexanal (134.7g, 1.05 moles) was heated at 70° C for 4 hours. The crude product was washed with water and evaporated to yield the diimine
10 (V) (220 g).

2. Reduction of the Diimine (V) with Sodium Borohydride

To a solution of 220 g diimine (V) in methanol (220 g) was added in small
15 portions sodium borohydride powder (20 g) until the reaction was complete as indicated by the disappearance of the imine carbon (168 ppm) in the ¹³C NMR spectrum. The product was washed with water and evaporated.

20 3. Methylation of Tris(secondary amine) compound (VI)

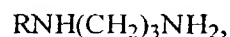
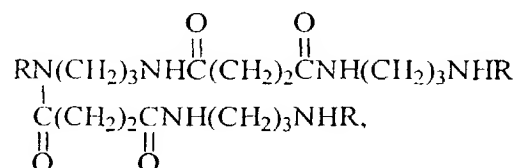
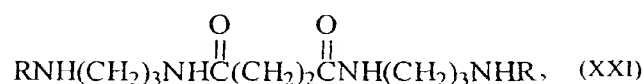
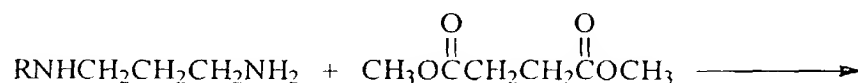
To compound VI was added with stirring 90% formic acid (149 g, 2.9 moles). The temperature was maintained at 50-60° C with cooling. A 37.1% formaldehyde solution (104 g, 1.286 moles) was added in small
25 portions. The resulting mixture was then evaporated on a rotary evaporator to remove the excess formic acid and formaldehyde. After the addition of concentrated HCl (1.4 mole), the mixture was heated at 70° C for 3 hours and was then neutralized with 25% aqueous NaOH solution. The product was separated, washed with water and evaporated. A pale
30 yellow liquid (208 g) was obtained.

4. Quaternization of the Tris(tertiary amine) Compound (VII)

Compound VII (140 g, 0.3 mole) dissolved in methanol (140 g), with
35 added NaHCO₃, was quaternized with methyl chloride at 80° C for 10

hours. The reaction was completed as indicated by disappearance of the methyl carbon (CH₃-N) peak in the ¹³C NMR spectrum. Filtration and evaporation of solvent yielded a pale yellow solid (VIII) (ca. 185 g).

5 Example 10 – Preparation of Multiple Functional Amidoamine Quaternary Ammonium Compounds: Reaction of Duomeen CD with dimethylsuccinate to form bis-Duomeen CD succinate [a bis(secondary amido-secondary amine) compound]



R = Coco

10

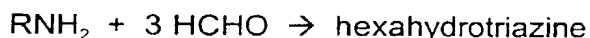
A mixture of Duomeen® CD (490.8 g, 2 equivalents of primary amine) and dimethyl succinate (136.08 g, 0.93 mole) was heated at 125-130°C under nitrogen for 5 hours. Additional dimethyl succinate (6.8 g, 0.046 mole) was added and the heating was continued for another 5 hours. The bis-Duomeen succinate (XXI), an off-white solid, was obtained. The product consisted of the bis-sec-amines (95% by weight) and unreacted Duomeen (4%).

15

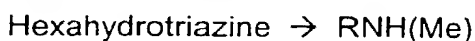
20 Methylation and quaternization of this bis-sec amine product can be performed in processes like those which have been described elsewhere in this application, to yield the bis(amido-amine) quaternary ammonium compound.

Example 11 – Alternative Route to Multiple Functional "Internal ester"
Quaternary Ammonium Compounds

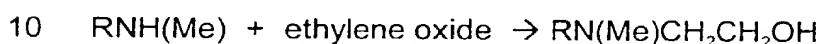
- Step 1: Reaction of a primary fatty amine compound with formaldehyde
5 will form the hexahydrotriazine intermediate;



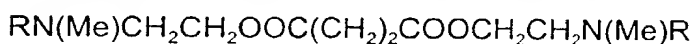
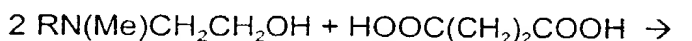
Step 2: hexahydrotriazine is reduced to form secondary amine;



Step 3: secondary amine is ethoxylated to form alcohol amine compound;

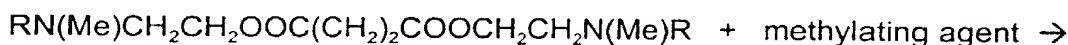


Step 4: two equivalents of ethoxylated amine react with dicarboxylic acid
to form Gemini tertiary amine;



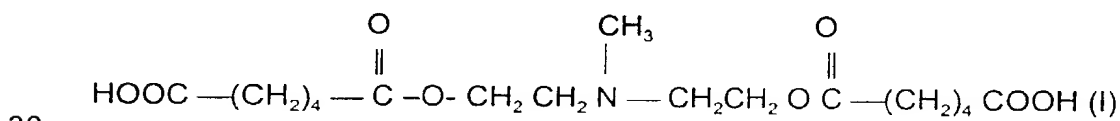
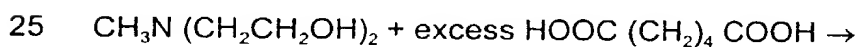
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Step 5: Gemini tertiary amine quaternized in reaction with methylating
agent (methyl chloride or methylsulfate).

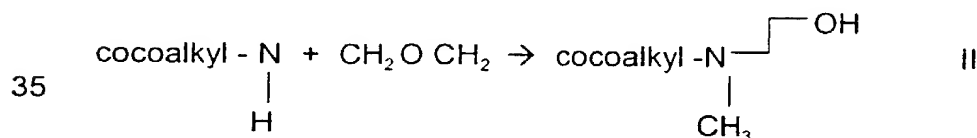


20 Gemini "internal ester" quaternary ammonium compound

Example 12 - Preparation of Ester - functional tris-quaternary ammonium
Compound step 1 preparation of diesteramine



step 2 Ethoxylation of long chain amino compound (see Example 7, step 1)

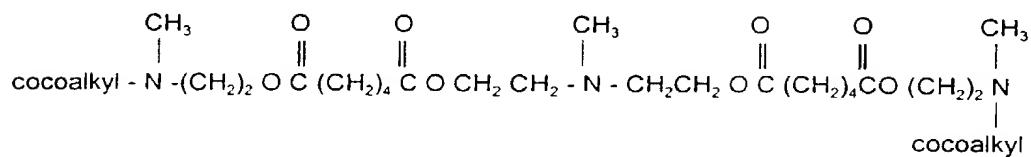


step 3 Reaction of ethoxylated amine compound II with dicarboxylic acid I, (see Example 7, step 2)

I + 2 II → followed by reductive methylation

5

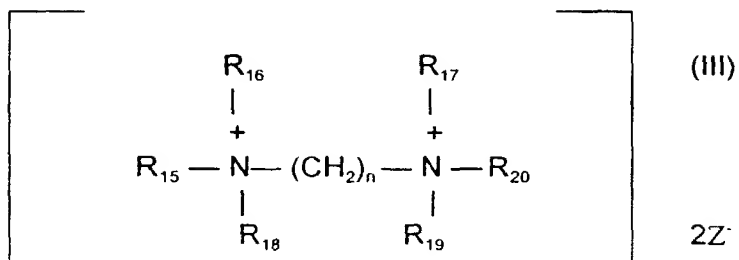
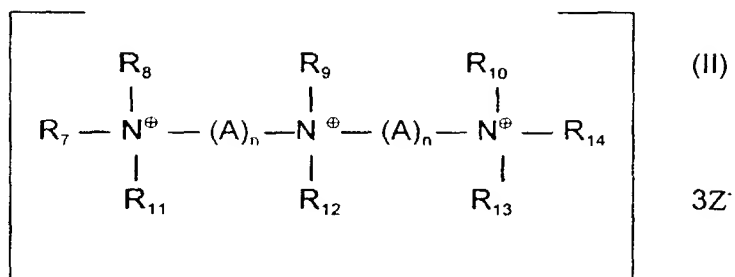
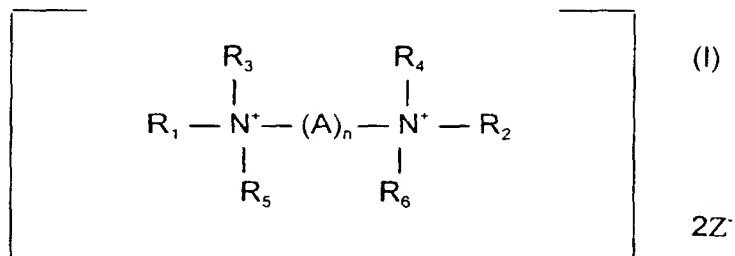
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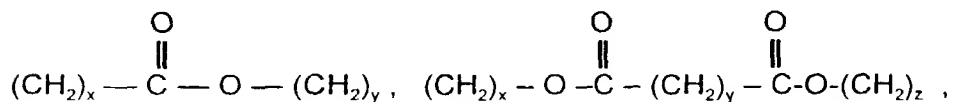
step 4 quaternization of III (see Example 7, step 3)

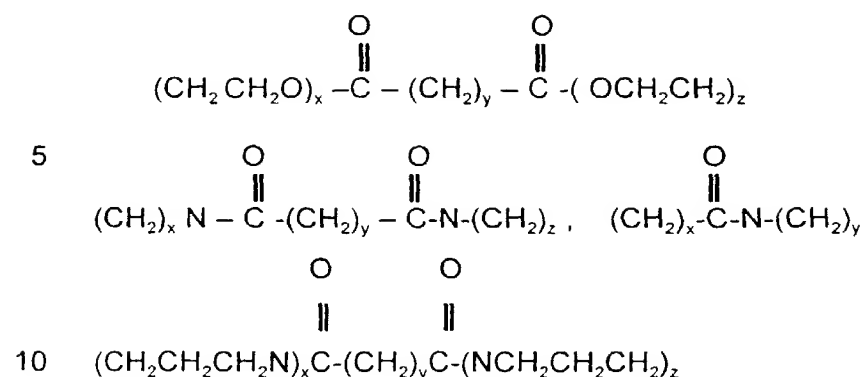
WE CLAIM:

1. A compound of general formula I, II or III:



wherein each of R_1 through R_{20} are independently selected from straight or branched chain, substituted or unsubstituted C_1 - C_{22} alkyl or alkenyl groups, wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage, or mixtures thereof; A is a spacer group of the formula:





or other ester- or amide-functional alkyl group, where x, y and z are each independently selected from an integer of from 1 to 20 and wherein in each of formulae I, II and III, Z⁻ is an anion, with the proviso that R₁₅ and R₂₀ are not the same.

2. The compound of claim 1 wherein that R₁, R₂, R₇, R₁₄, R₁₅, and R₂₀ are each independently selected from the group consisting of C₁₂-C₁₈ alkyl groups, C₁₂ - C₁₈ alkyl groups containing an ester linkage and C₁₂ - C₁₈ alkyl groups containing an amide linking group.

3. The compound of claim 1 wherein each of R₁, R₂, R₃, R₄, R₅, and R₆ are selected from the group consisting of methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, C₁₃ - C₁₅ mixed alkyl group, dodecylalkyl, octadecylalkyl, oleylalkyl, cocoalkyl, soyaalkyl, tallowalkyl, hydrogenatedtallowalkyl and mixtures thereof; and n is an integer of from 1 to 5.

4. The compound of claim 1 wherein each of R₇, R₈, R₉, R₁₀, R₁₁, R₁₂, R₁₃ and R₁₄ are independently selected from the group consisting of methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, a C₁₃ - C₁₅ mixed alkyl group, dodecylalkyl, octadecylalkyl, oleylalkyl, cocoalkyl, soyaalkyl, tallowalkyl, hydrogenatedtallowalkyl and mixtures thereof; and that n is an integer of from 1 to 5.

5. The compound of claim 1 wherein each of R_{15} , R_{16} , R_{17} , R_{18} , R_{19} and R_{20} is independently selected from the group consisting of methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, a $C_{13} - C_{15}$ mixed alkyl group, dodecylalkyl, octadecylalkyl, oleylalkyl, cocoalkyl, soyaalkyl, tallowalkyl, hydrogenated
 5 tallowalkyl and mixtures thereof with the proviso that R_{15} is not the same as R_{20} ; and n is an integer of from 1-20.

6. A surfactant composition which comprises at least one of the compounds of claim 1.

10 7. A process for preparing the multiple functional quaternary ammonium compounds of general Formula I which comprises reacting a dialkylalkanol amine of formula



wherein each of Q_1 , Q_2 and Q_3 is independently selected from the group consisting of C_1 - C_{22} alkyl groups and a dicarboxylic acid of the formula



20 wherein n is an integer of from 1-10, to form a reaction mixture and thereafter quaternizing the reaction mixture.

8. The process of claim 7 wherein said dialkylalkanol amine is prepared by ethoxylating a fatty amine compound of the formula



wherein Z is a C_{12} - C_{22} substituted or unsubstituted, saturated or unsaturated, straight or branched chain alkyl group, and Y is a C_1 - C_{22} substituted or unsubstituted, saturated or unsaturated, straight or branched chain alkyl group.

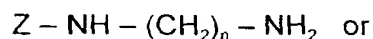
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9. The process of claim 8 wherein said fatty amine compound is selected from the group consisting of dodecylamine, hexadecylamine, octadecylamine, oleylamine, cocoalkylamine, soyaalkylamine, tallowalkylamine, hydrogenatedtallowalkyl amine, dicocoalkylamine, ditallowalkylamine, dihydrogenated tallowalkylamine, dioctadecylamine, and mixtures thereof, and the quaternizing agent is a methylating agent.

10. The process of claim 7 wherein the dialkylalkanol amine is selected from the group consisting of dimethylethanolamine, diethylethanol amine, and mixtures thereof; and the dicarboxylic acid is selected from the group consisting of oxalic, malonic, succinic, glutaric, adipic, maleic, fumaric and mixtures thereof, and the quaternizing agent is a long chain alkylhalide reagent.

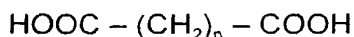
11. The process of claim 10 wherein the dialkylalkanolamine is dimethylethanolamine and the dicarboxylic acid is adipic acid.

12. A process for preparing multiple functional hydrophilic/hydrophobic compounds which comprises reacting a diamine of the formula:



a triamine or tetramine of the formula: $Z - NH - (CH_2CH_2CH_2NH)_m$
 $CH_2CH_2CH_2NH_2$ where Z is a $C_1 - C_{22}$ saturated or unsaturated alkyl group and m is 1 or 2,

with a dicarboxylic acid of the formula:



wherein n is an integer of from 1-10.

13. The process of claim 12 wherein Z is selected from cocoalkyl, tallow alkyl, or oleylalkyl, and the dicarboxylic acid is selected from the

group consisting of oxalic, malonic, succinic, glutaric, adipic, maleic, fumaric and mixtures thereof.

14. The process of claim 13 wherein the amine is selected from the group consisting of N-coco 1,3 – diaminopropane, N-tallow –1,3 diaminopropane, N,N,N' – trimethyl-N-tallow-1,3 diaminopropane, N-oleyl-1,3 diaminopropane, 3 –tallowalkyl-1,3-hexahydropyrimidine, N-tallowalkyl dipropylene triamine, N-tallowalkyl tripropylene tetramine and mixtures thereof, and the dicarboxylic acid is selected from the group consisting of oxalic, malonic, succinic, glutaric, adipic, maleic, fumaric and mixtures thereof.

15. The compound of claim 1 wherein R_{15} and R_{20} are each independently selected from the group consisting of C_{12} - C_{18} alkyl groups, methyl, ethyl, propyl, 2-ethylhexyl, nonylalkyl, and C_{13} - C_{15} mixed alkyl group, dodecylalkyl, octadecylalkyl, oleylalkyl, cocoalkyl, soyaalkyl, tallowalkyl, hydrogenatedtallowalkyl and C_{12} - C_{18} alkyl groups containing an ester or amide function ; and n is an integer of from 2 to 3.

16. The compound of claim 1 wherein R_{16} , R_{17} , R_{18} , R_{19} are independently selected from the group consisting of methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, and a C_{12} - C_{18} mixed alkyl group; and n is an integer of from 2 to 3.

17. A viscosity modifying agent comprising the compound of claim 15.

18. A viscosity modifying agent comprising the compound of claim 16.

19. The compound of claim 1 wherein R_{15} and R_{20} are each independently selected from the group consisting of C_{12} - C_{18} alkyl groups, methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, and a C_{12} - C_{18} mixed alkyl

group and C₁₂-C₁₈ alkyl groups containing an ester or amide function; and n is an integer of from 5 to 8.

20. The compound of claim 1 wherein R₁₆, R₁₇, R₁₈, R₁₉ are independently selected from the group consisting of methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, and a C₁₂-C₁₈ mixed alkyl group; and n is an integer of from 5 to 8.

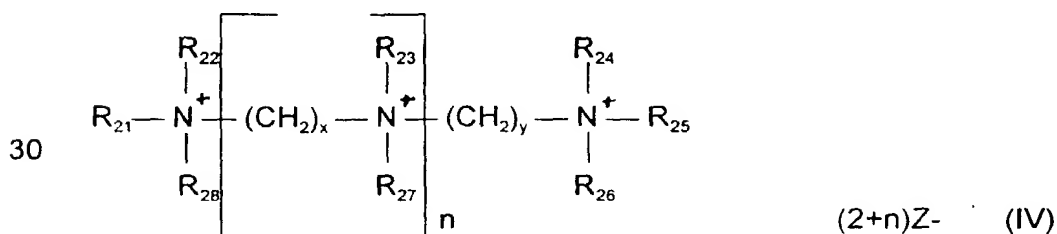
21. The compound of claim 1 wherein R₁₅ and R₂₀ are each independently selected from the group consisting of C₁₂-C₁₈ alkyl groups, methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, and a C₁₂-C₁₈ mixed alkyl group and C₁₂-C₁₈ alkyl groups containing an ester or amide function, and n is an integer of from 2 to 20.

22. An ore flotation aid comprising the compound of claim 21.

23. The ore flotation aid of claim 22 wherein in said compound R₁₅ and R₂₀ are each independently selected from the group consisting of C₁₂-C₁₈ alkyl groups, and C₁₂-C₁₈ alkenyl groups, and C₁₂-C₁₈ alkyl groups containing an ester or amide function; R₁₆, R₁₇, R₁₈, R₁₉ are methyl groups; and n is an integer of from 2 to 12.

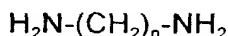
24. A calcium ore flotation aid comprising the compound of claim 23.

25. A process for the preparation of compounds of general formula IV



wherein R_{21} , R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , and R_{28} are the same or different and are selected from straight or branched chain, substituted, or unsubstituted C_1 - C_{22} alkyl or alkenyl groups, wherein said alkyl or alkenyl groups optionally contain at least one ester linkage, at least one amide linkage or mixtures thereof, and where x and y are each independently an integer of from 1-20, n is 1-20 and Z^- is an anion, said process comprising the reaction of a polyaminoalkyl compound with multiple equivalents of alkyl or alkenyl aldehyde or alcohol compounds.

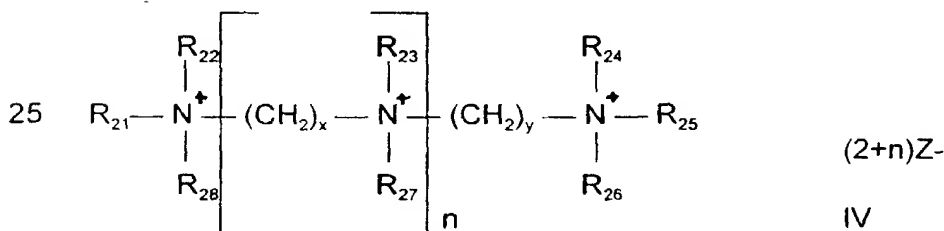
26. The process of claim 25 wherein the diaminoalkyl compound is a compound of the formula:



and the aldehyde or alcohol compound is selected from the group consisting of methyl, ethyl, propyl, 2-ethylhexyl, nonyl-alkyl, C_{12} - C_{18} mixed alkyl groups and mixtures thereof and n is an integer of from 1 to 5.

27. The process of claim 25 wherein the diaminoalkyl compound is hexamethylenediamine.

28. A compound of formula IV



wherein R_{21} , R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , and R_{28} are the same or different and are selected from straight or branched chain, substituted, or unsubstituted C_1 - C_{22} alkyl or alkenyl groups, wherein said alkyl or alkenyl

groups optionally contain at least one ester linkage, at least one amide linkage or mixtures thereof, and where x and y are each independently an integer of from 1-20, n is greater than 1 and Z⁻ is an anion.

- 5 29. A surfactant composition which comprises at least one compound of claim 1 in combination with at least one conventional surfactant.

30. The composition of claim 29 wherein said conventional surfactant is a mono- quaternary ammonium compound.

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31. A surfactant composition which comprises at least one compound of claim 28 in combination with at least one conventional surfactant.

- 15 32. The composition of claim 31 wherein said conventional surfactant is a mono- quaternary ammonium compound.

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: CATIONIC GEMINI AND RELATED MULTIPLE HYDROPHILIC/HYDROPHOBIC FUNCTIONAL COMPOUNDS AND THEIR USE AS SURFACTANTS

the specification of which:

☒ was filed on 30 December 1999 as Appln. Ser. No. PCT/US99/31246

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. All factual statements made in the specification of my own knowledge are true and all factual statements made on information and belief are believed to be true.

I acknowledge to the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Sec. 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Priority Claimed

(Number) (Country) (Day/Month/Year) Yes No

I hereby claim the benefit under Title 35, United States Code § 119 of any provisional application(s) listed below:

<u>60/114,544</u>	<u>U.S.</u>	<u>31 December 1998</u>
Appln. Ser. No.	Country	Day/Month Year

ACR6100P1US

I hereby claim the benefit under Title 35, United States Code, Sec. 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec. 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Sec. 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Appln. Ser. No.)

(Filing Date)

(Status: patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following as my attorneys of record, with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Sec. 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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